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CONSTRUCTION MATERIAL COATING COMPOSITION

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CONSTRUCTIONAL MATERIAL COATING COMPOSITION
[Ken zai yo toryo sosei butsu]

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Claim

/1*

A construction material coating composition containing a modified acryl copolymer characterized by the fact that 0-60 wt % of an aromatic type vinyl monomer, 5-25 wt % of a vinyl type monomer containing an epoxy group, 0-10 wt % of alkyd having a copolymerizable unsaturated bond, and 5-95 wt % another vinyl type monomer copolymerizable with these are copolymerized, and then, with respect to 100 parts by weight of the acryl copolymer containing epoxy groups obtained in this manner, fatty acid is allowed to undergo an addition reaction at a ratio of 5-60 parts by weight.

* [Numbers in the margin indicate pagination of the original foreign language text.]

Detailed explanation of the invention

Objective of the invention

The present invention relates to a primer for use in construction materials with good permeation characteristics, alkali resistance, and solvent resistance, and a top coat for use in construction materials with good weatherability, gloss and physical properties.

Industrial application field

During the application of a coating on cement, slate, mortar or other alkaline inorganic base materials, it is common to coat a primer (a sealer) by sealing the alkali flowing out from these base materials for the purpose of the prevention of the deterioration of the intermediate coating or the top coating. As the required characteristics of these primers, good alkali resistance and water resistance, freedom from being attacked by a solvent in the case of using a solvent type coating material in the top coating, and good interlayer adherence between the intermediate coating and the top coating can be mentioned.

Furthermore, recently, mainly in the case of the repairs of building structures, by sealing or coating light cracks, spalling or other defect portions on outside walls, interior walls and so on, a material for encroaching the sealer into the defect portions and preventing deterioration, a so-called permeating sealer, is highly desirable. In order to render the permeation characteristics, it is effective to decrease the molecular weight and/or Tg. However, a resin with low molecular weight or Tg is always markedly low in alkali resistance and solvent resistance.

On the other hand, as top coats for use in construction materials, vinyl acetate-acryl type coating material, acryl-styrene type coating material as one-liquid lacquers, or two-liquid type isocyanate curing acryl coating material have been widely used. The two-liquid type coating material is very good in performance. However, there are problems in the aspects of operability, toxicity, and cost. The lacquer type generally has a low cost. Since it is not a crosslinked three-dimensional coated film, it is common that there has been deterioration in performance, especially weatherability, general physical properties, and adherence characteristics.

Effect of the invention

As a result of diligent research into these points, the present inventors have discovered that the modified acryl copolymer obtained by the addition of fatty acid into a copolymer containing an epoxy group has good dilution characteristics with respect to water. Furthermore, if the molecular weight is set low to a certain extent, the permeation characteristics are better than the conventional lacquer resin. Furthermore, by the oxidative polymerization of unsaturated bonds contained in fatty acid of said modified acryl copolymer, since a strong coated film with a high molecular weight is rendered, water resistance, alkali resistance and solvent resistance are

good. Since the interlayer adherence with an intermediate coating material like that of an emulsion type or the like is good, it is most appropriate as a sealer. Furthermore, it has been discovered that, if said modified acryl copolymer is used as a top coating resin for construction materials, weatherability and general physical properties are good by oxidative polymerization. Moreover, the gloss is very good in comparison to the conventional acryl lacquer. Thus, the present invention has been accomplished. Furthermore, in the stage of the addition of fatty acid into the copolymer containing an epoxy group, since a hydroxyl group is formed, urethane crosslinking can be achieved if a polyisocyanate is blended in. The two crosslinking reactions by oxidative polymerization crosslinking with a dryer and the urethane crosslinking can be used in combination.

Prior art

However, the method for obtaining an air-curing resin by the addition of a dry type oil fatty acid into such an acryl copolymer containing an epoxy group has already been disclosed in British Patent No. 767476. Furthermore, in order to eliminate the disadvantage in gloss insufficiency due to wetting insufficiency with respect to the pigment for the resin obtained by such a method are the improved methods described in Japanese Kokai Patent Applications Nos. Sho 53 [1978]-51233 and Sho 53 [1978]-99231.

However, in any of the improved methods described previously, after the addition of the dry type oil fatty acid into the glycidyl group in the acryl resin, since it is a method for esterification with a dicarboxylic acid anhydride like tetrahydrophthalic acid anhydride, it causes a prolonging of the overall reaction time and complicates the reaction control consisting of three stages of (1) the manufacture of the acryl copolymer, (2) the addition of the dry type oil fatty acid into said copolymer, and (3) the esterification of said fatty acid modified copolymer and the dicarboxylic acid anhydride. Since the production cost is increased, it cannot be said to be a preferred method.

Constitution of the invention

In view of the actual situations described previously, the present inventors have obtained a fatty acid modified acryl copolymer with good wetting characteristics with respect to a pigment and excellent gloss by a simple and convenient method.

In other words, the present invention provides a construction material coating composition containing a modified acryl copolymer characterized by the fact that 0-60 wt % of an aromatic type vinyl monomer, 5-25 wt % of a vinyl type monomer containing an epoxy group, 0-10 wt % of alkyd having a copolymerizable unsaturated bond, and 5-95 wt % of another vinyl type monomer copolymerizable with these are copolymerized, and then, with respect to

100 parts by weight of the acryl copolymer containing epoxy groups obtained in this manner, fatty acid is allowed to undergo on addition reaction at a ratio of 5-60 parts by weight.

As fatty acids that can be used in the present invention, in the typical ones, cotton seed oil, soybean oil, rice bran oil, dehydrated castor oil, linseed oil, tall oil, Chinese tung oil other natural oils and fats, or other dry type oil fatty acids, or "Hygen" [transliteration], "Hygen H," "Hygen S," "SK. Conjugated Fatty Acid # 20" (These are products of General Research Chemical Co., Ltd.), or "Pamolyn 200, 300" (products of U. S. Hercules Co.) or other synthetic dry type oil fatty acids, or coconut oil fatty acid, castor oil fatty acid, octylic acid, lauric acid, "Versatic [transliteration] acid" (a synthetic dry type oil fatty acid manufactured by Dutch Shell Co.), stearic acid, hydroxyl stearic acid or other fatty acids with an iodine value less than 100 or saturated fatty acids and so on are available. Of course, these semi-dry type oils, non dry type oils, and saturated fatty acids can be used by mixing with the dry type oil fatty acids as those mentioned previously.

As the amount of usage of the fatty acids as mentioned previously, a ratio of 5-60 parts by weight, preferably 10-50 parts by weight, with respect to 100 parts by weight of the vinyl copolymer containing an epoxy group mentioned previously is appropriate.

In the case in which this amount of usage is less than 5 parts by weight, physical properties or solvent resistance will deteriorate. On the other hand, in the case in which it is more than 60 parts by weight, yellowing will occur easily and weatherability will also decrease. In addition, as a result of the excessive proceeding of the crosslinking of the coated film obtained, bending characteristics are damaged. It becomes a brittle coated film and cannot be supplied for practical use in any case.

Next, a description will be given in regard to the vinyl copolymer containing an epoxy group mentioned previously. As the vinyl copolymers containing epoxy groups, in the typical ones, polymerized compounds containing epoxy groups obtained by the addition reaction at an equal molar ratio of "Epichlon [transliteration] 200, 400, 441, 850 or 1050" (epoxy resins manufactured by Dai Nippon Ink Chem. Ind. Co., Ltd.), "Epicoat [transliteration] 828, 1001 or 1004" (epoxy resins manufactured by Shell Co.), "Araldite [transliteration] 6071 or 6084" (epoxy resins manufactured by Swiss Ciba Geigy Co.), "Chissonox [transliteration] 221" (an epoxy compound manufactured by Chisso Co., Ltd.) or "Denacol [transliteration] BX-810" (an epoxy compound manufactured by Nagase Ind. Co., Ltd.), or a variety of other poly epoxy compounds having at least two or more epoxy groups in one molecule, in a variety of unsaturated carboxylic acids like the addition products obtained by the equal molar addition reaction of starting with glycidyl (meth)acrylate, β -methyl glycidyl (meth)acrylate, and (meth)acryl glycidyl ether, (meth)acrylic acid, fumaric acid, maleic acid, itaconic acid or other unsaturated monomers or dicarboxylic acids, mono esters of such unsaturated dicarboxylic acids and monohydric

alcohols, other α , β -ethylenic unsaturated carboxylic acids, "HOA-MP" or "HOA-HS" (these being acryl monomers containing carboxyl groups manufactured by Osaka Organic Chemical Co., Ltd.) or other compounds containing carboxyl groups, or mono-2-(meth)acryloyl oxy ethyl phthalate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, di-2-hydroxyethyl fumarate, or other vinyl monomers containing hydroxyl groups, with maleic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, benzene tricarboxylic acid, "Hymic [transliteration] acid" (a product of Hitachi Kasei Ind. Co., Ltd.), dodecynyl succinate, succinic acid, tetrachloro phthalic acid or other polycarboxylic acids (anhydrides) and so on are available. These can be used alone or after mixing of two or more. If the reactivity, the number of reaction processes, the viscosity of the final product, the price and so on are considered, glycidyl (meth)acrylate, β -methyl glycidyl (meth)acrylate, or other monomers of the type of the relatively low molecular weights can be used most easily. /3

Said vinyl monomers containing epoxy groups are used in the range of 5-25 wt %. It goes without saying that, since the epoxy groups inside said monomers are rendered in the reaction with the fatty acid as disclosed previously, the amount of usage of said monomers is to be determined mainly in dependence on the amount of usage of this fatty acid. In general, they are used at a ratio of the epoxy groups in the range of 1.0-1.25 equivalents per equivalent of this fatty acid carboxyl group. This is preferred from the aspect of the reaction rate and the aspect of the prevention of the adverse effect of the residual epoxy groups on the coated film.

Furthermore, the alkyd resin having the copolymerizable unsaturated bonds mentioned previously, not to speak of pigments with a small oil absorption amount like titanium oxide and red iron oxide, is used in the case of the improvement of the dispersibility of pigments having a relatively poor dispersibility and a relatively large oil absorption amount like, in particular, organic pigments of the quinacridone type, the phthalocyanine type, azo type and so on, or carbon black. In this sense, it can be said that said alkyd resin itself is not much related to coated film performance.

As said alkyd resin, any material modified with oil or a fatty acid, or a material not modified by these, the so-called oil-free alkyd resin, can be used. However, in the present invention, among the these various alkyd resins, in particular, those of the type having unsaturated bonds having copolymerizing characteristics with various vinyl monomers are appropriate in the present invention.

As said alkyd resins, those obtained by reaction by the ordinary method for octylic acid, lauric acid, stearic acid, "Versatic acid" or other saturated fatty acids; oleic acid, linolic acid, linoleinic acid, eleostearic acid, ricinolic acid or other unsaturated fatty acids; by using or not using one or a mixture of "Pamolyn 200, 300," Chinese tung oil (fatty acid), linseed oil (fatty acid), dehydrated castor oil (fatty acid), tall oil (fatty acid), cotton seed oil (fatty acid), soybean

oil (fatty acid), olive oil (fatty acid), safflower oil (fatty acid), castor oil (fatty acid), rice bran oil (fatty acid), or other (semi) dry type oils (fatty acids), hydrogenated coconut oil (fatty acid), coconut oil (fatty acid), palm oil (fatty acid), or other non dry oils (fatty acids), or other oils or fatty acids, by the ordinary method for one or more of ethylene glycol, propylene glycol, glycerin, trimethylol ethane, trimethylol propane, neopentyl glycol, 1, 6-hexane diol, 1, 2, 6-hexane triol, pentaerythritol, sorbitol or other polyhydric alcohols, with one or more of benzoic acid, p-t-butyl benzoic acid, phthalic acid (anhydride), hexahydro phthalic acid (anhydride), tetrahydro phthalic acid (anhydride), phthalic acid, tetrachloro phthalic acid (anhydride), hexachloro phthalic acid (anhydride), tetrabromo phthalic acid (anhydride), trimellitic acid, "Hymic acid," Succinic acid (anhydride), maleic acid (anhydride), itaconic acid (anhydride), fumaric acid, adipic acid, sebacic acid, oxalic acid or other carboxylic acids, and if necessary, "Cardura [transliterated] E" (a product of Shell Co.) or other glycidyl esters of fatty acids as mono epoxy compounds, "Epichlon [transliteration] 200, 400," "Epichlon 828, 1001" or other polyepoxy compounds, or triline [transliteration] diisocyanate, hexamethylene diisocyanate, isophorone, 4, 4'-methylene bis (cyclohexyl isocyanate) or other diisocyanates, polyisocyanates obtained from the addition reaction of these various diisocyanates with the polyhydric alcohols mentioned previously of water, or polyisocyanates having isocyanuric rings obtained by the (co)polymerization of diisocyanate alone or two or more are appropriate by the substitution of a portion of the polyhydric alcohols or carboxylic acids mentioned previously.

At this time, in regard to those having no polymerizable unsaturated bonds as said alkyd resin or being of the little saturated fatty acids or non dry type oils (fatty acids), or being of the type of oil-free alkyd resin not modified with oils or fatty acids, it goes without saying that the introduction of polymerizable unsaturated bonds as graft points of other various vinyl monomers into said alkyd resin by using maleic acid (anhydride), fumaric or other unsaturated carboxylic acids is required. /4

Said alkyd resin obtained in this manner is used in the range of 0-10 wt %. When it is used at a large amount of more than 10 wt %, solvent resistance, contamination resistance and so on will deteriorate. Furthermore, during polymerization, the carboxyl group inside said alkyd resin and the epoxy group inside the vinyl monomers containing epoxy groups mentioned previously will react to form a gel easily, or other disadvantages will appear in an undesirable manner.

Therefore, as the amount of usage of said alkyd resin, within the range as mentioned previously, it is advisable that the decision is made by taking into consideration the acid value, oil length, the amount of the polymerizable unsaturated bonds as well as the molecular weight of said alkyd resin, the molecular weight of the modified copolymer obtained and so on so that gelation due to the reaction of these groups with each other does not occur.

As the aromatic type vinyl monomers mentioned previously, the typical ones, styrene, α -methyl styrene, p-t-butyl styrene, vinyl toluene and so on are available. Among these, styrene is the best from the aspect of cost.

When the amount of said aromatic type vinyl monomers is used at a large amount of more than 60 wt %, the weatherability of the coated film will deteriorate and it is not suitable as a coating material resin for outdoor use. Therefore, in the case of usage, in less than 60 wt %, it is to be decided appropriately according to gloss, durability, weatherability or other required performances. For a balance in gloss, muscle-holding feeling, leveling characteristics and weatherability, a range of 10-50 wt % is preferred.

As typical vinyl monomers containing epoxy groups, the aromatic type vinyl monomers and other vinyl monomers copolymerizable with alkyd resins having copolymerizable unsaturated bonds mentioned previously, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, dibromopropyl (meth)acrylate, tribromophenyl (meth)acrylate, alkoxy alkyl (meth)acrylate or a variety of other (meth)acrylates; diesters of maleic acid, fumaric acid, itaconic acid or other unsaturated dicarboxylic acids and monohydric alcohols; vinyl acetate, vinyl benzoate, "Veoba" [transliteration] (vinyl ester manufactured by Shell Co.) or other vinyl esters; "Viscoat" [transliteration] BF, BFM, 3F or 3FM" (chlorine-containing acryl monomers manufactured by Osaka Organic Chem. Co., Ltd.), perfluoro cyclohexyl (meth)acrylate, diperfluoro cyclohexyl fumarate, N-1-propyl perfluoro octane sulfonamide ethyl (meth)acrylate, or other vinyl esters containing (per)fluoro alkyl groups, vinyl ethers, (meth)acrylates, unsaturated carboxylic acid esters or other fluorine-containing compounds; or (meth)acrylonitrile, vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, or other olefins are available.

As typical vinyl monomers containing hydroxyl groups, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, di-2-hydroxyethyl fumarate, mono-2-hydroxyethyl monobutyl fumarate, polyethylene glycol mono (meth)acrylate, or other hydroxyl alkyl esters of α , β -ethylenic unsaturated carboxylic acids; (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid or other unsaturated monomers or dicarboxylic acid as a start, mono esters of these dicarboxylic acids with monohydric alcohols, or other α , β -ethylenic unsaturated carboxylic acids; adducts of the previously mentioned α , β -unsaturated carboxylic acid hydroalkyl esters and previously mentioned various polycarboxylic acids (anhydrides), as well as adducts with "Cardura E," coconut oil fatty acid glycidyl ester, octylic

acid glycidyl ester or other mono glycidyl esters of monohydric carboxylic acids, or butyl glycidyl ether, ethylene oxide, propylene oxide or other mono epoxy compounds; or N-methylol acrylamide or other compounds containing methylol groups, hydroxyethyl vinyl ether and so on are available. Of course, it is necessary to decide the amount of usage so that gelation will not be reached in such vinyl monomers containing hydroxyl groups or other monomers containing functional groups. The amounts are to be decided so that gelation due to the reaction between the hydroxyl groups inside said vinyl monomers containing hydroxyl groups and the (β -methyl) glycidyl groups inside the (β -methyl) glycidyl (meth)acrylate mentioned previously does not occur.

In obtaining the composition of the present invention, first of all, the vinyl copolymer containing an epoxy group mentioned previously is generally prepared by solution polymerization. To this copolymer, the dry type oil fatty acid mentioned previously is rendered. However, in this copolymerization reaction also called the first stage reaction, as long as the polymer conversion of the vinyl copolymer containing an epoxy group is maintained at more than 95 % in general, even without waiting for the completion of said copolymerization, the dry type oil fatty acid is added and the addition reaction also called the second stage reaction can proceed. /5

Furthermore, there are no special restrictions to be imposed on the reaction temperature. It is acceptable as long as it is a temperature appropriate for the polymerization of the various component compounds mentioned previously during the copolymerization reaction, that is, it is within the range of 50-140°C. On the other hand, during the addition reaction, it is acceptable as long as it is a temperature appropriate for the addition of the various component compounds as those mentioned previously during the addition reaction, that is, it is within the range of 110-180°C. In particular, during the addition reaction, it is also possible to increase the temperature in order to promote this reaction.

Moreover, it is also possible to use a ring opening catalyst for the epoxy group in order to promote the addition reaction. In this case, any of the publicly known customarily used catalysts can be utilized. Among these, in the especially typical ones, triethylamine, diethylene triamine, imidazole or other tertiary amines, BF_3 complex, phosphoric acid, sulfuric acid or other acids are available.

Furthermore, as polymerization initiators for use during the conduction of polymerization, any of the publicly known customarily used ones can be utilized. Among these, if the especially typical ones are exemplified, azo bis isobutyronitrile, benzoyl peroxide, t-butyl perbenzoate, t-butyl peroctate, di-t-butyl peroxide and so on are available. Furthermore, a chain transfer agent can also be used in combination.

As the solvents, the publicly known customarily used ones can also be utilized. If the especially typical ones are exemplified, toluene, xylene or other aromatic type solvents, ethyl acetate, butyl acetate, Cellosolve acetate, or other ester type solvents, methanol, butanol or other alcohol type solvents, methyl ethyl ketone, methyl isobutyl ketone or other ketone type solvents and so on are available. Furthermore, hexane, heptane, cyclohexane, methyl cyclohexane, petroleum naphtha, mineral spirit or other aliphatic or alicyclic type solvents can also be used.

As regards the type of such solvents, their combination and the amount of usage, an appropriate decision can be made by taking into consideration the amount of usage of the fatty acid mentioned previously, the amount of usage of the vinyl portion in the vinyl copolymer containing an epoxy group and so on.

Since the fatty acid modified vinyl copolymer obtained in this manner has both the double bond and the hydroxyl group in the molecule, it can be carried out by oxidative polymerization with a dryer and urethane crosslinking alone and in combination.

As the dryer that can be used here, in general, any of those customarily used for coating materials are acceptable. Among these, as the especially typical ones, naphthenates, octylates, resonates and so on of cobalt, vanadium, manganese, cerium, lead, iron, calcium, zinc, zirconium, nickel, tin or the like are available. Its amount of usage can be decided appropriately according to the type of this dryer, the combination of the various components, the required performance and so on from the customarily used amounts.

At this time, it is also possible to increase the usage effectiveness of said dryer by using a small amount of benzoyl peroxide, methyl ethyl ketone peroxide, t-butyl perbenzoate or other organic peroxides in combination. Furthermore, it is also possible to use a leveling agent or other publicly known customarily used coating material additives in combination.

Furthermore, as a typical polyisocyanate, triline diisocyanate, xylylene diisocyanate, diphenyl methane diisocyanate, or other aromatic diisocyanates; tetramethylene diisocyanate, hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate, or other aliphatic diisocyanates; isophorone diisocyanate, methyl cyclohexane-2, 4-(or 2, 6-) diisocyanate, 4, 4'-methylene bis (cyclohexyl isocyanate), 1, 3-di(isocyanate methyl) cyclohexane or other alicyclic diisocyanates or other diisocyanates, or adducts of these various diisocyanates and previously mentioned polyhydric alcohols, low molecular weight polyester type resins having functional groups reacting with isocyanate groups (also including those of the oil modified type), acryl type copolymers (also including those using styrene as a co-monomer component), water or the like, as well as burette [transliteration] bodies, (co)polymers (also including oligomers) of the various diisocyanates mentioned previously and so on are available.

However, in using said polyisocyanate, the usage of an aromatic diisocyanate or its derivative that becomes yellow due to ultraviolet light or undergoes cracking is not appropriate

for the top coating. Therefore, in this case, for use as a top coating, it is acceptable to use an aliphatic diisocyanate, an alicyclic diisocyanate or their various derivatives or the like having good weatherability.

As the amount of usage of said polyisocyanate, an equivalence ratio of $\text{OH/NCO} = 1/0.1$ to $1/1.2$ is appropriate.

The composition of the present invention is in agreement with a variety of major desires in said industry as described above. The three types of the crosslinking reactions consisting of the crosslinking reaction due to the oxidative polymerization on the basis of the fatty acid residual groups contained inside the modified copolymer, the crosslinking reaction between the hydroxyl groups present to a certain extent inside the modified copolymer and the polyisocyanate blended with respect to this, and the crosslinking reaction of these two can be adopted according to the desired reaction in regard to one type of the modified vinyl copolymer. Furthermore, a specific composition capable of obtaining a coated film with an excellent performance can be achieved through such a crosslinking reaction. /6

Next, the present invention will be explained more specifically with application examples and comparative examples. In the following, "parts" and "%" are all based on a weight basis unless specified otherwise.

(1) Application examples and comparative examples related to primers

Application Example 1

In a 4-neck flask provided with a thermometer, a reflux cooler, a stirrer and a nitrogen gas inlet, 800 parts of xylene, 71 parts of "Beckosol [transliterated] P-470-70" (a long oil alkyd resin manufactured by Dai Nippon Ink Chem. Ind. Co., Ltd.) and 2 parts of di-t-butyl peroxide (to be abbreviated to DTBPO hereafter) were charged and heated to 125°C . When the same temperature was reached, a mixture consisting of 400 parts of styrene (St), 300 parts of methyl methacrylate (MMA), 55 parts of acrylonitrile (AN), 125 parts of glycidyl methacrylate (GMA), 70 parts of ethyl acrylate (EA), 10 parts of azo bis isobutyronitrile (AIBN), 10 parts of t-butyl peroxate (TBPO), and 10 parts of t-butyl perbenzoate (TBPB) was added dropwise in 5 h. After the completion of the dropwise addition, it was kept at the same temperature for 5 h. When the nonvolatile matter content was 53.9 %, 50 parts of linseed oil fatty acid, 150 parts of soybean oil fatty acid, and 0.2 parts of 2-methyl imidazole (2MIZ) were added. At the same temperature, the addition reaction of the glycidyl group and the carboxyl group was carried out for 13 h. A solution of a fatty acid modified acryl copolymer with a nonvolatile matter content of 60.3 %, a viscosity (Gardner; the same hereafter) of Z_6 , and an acid value of 2.6 was obtained. The nonvolatile matter content was adjusted to 50 % by the addition of 400 parts of xylene to this material.

The resin solution obtained in this manner was a transparent solution with a nonvolatile matter content of 50.1 %, a viscosity of L-M, a color number (Gardner; the same hereafter) of 5-6, and a number average molecular weight (the same hereafter) of 4000 by the gel permeation chromatography (GPC).

Application Example 2

In the same flask as that in Application Example 1, 200 parts of "Beckosol 1343" (a medium oil alkyd resin manufactured by the same company as that mentioned previously), 1300 parts of xylene, and 3 parts of DTBPO were charged and heated to 120°C. At the same temperature, a mixture consisting of 300 parts of St, 300 parts of MMA, 200 parts of GMA, 100 parts of n-butyl acrylate (BA), 15 parts of AIBN, 10 parts of TBPO, and 2 parts of TBPB was added dropwise in 5 h. Furthermore, it was kept at the same temperature for 12 hr. The polymerization was continued, and an acryl copolymer with a nonvolatile matter content of 42.0 % and a viscosity of Y was obtained.

Next, to this copolymer, 100 parts of cotton seed oil fatty acid and 300 parts of dehydrated castor oil fatty acid were added. At 150°C, the reaction was carried out until the acid value was about 1. A transparent resin solution with a nonvolatile matter content of 50.8 %, a viscosity of Z-Z [subscript illegible], an acid value of 1.1, a color number of 1-2, and a number average molecular weight of 7200 was obtained.

Application Example 3

In the same flask as that in Application Example 1, 1300 parts of xylene and 3 parts of DTBPO were charged and heated to 120°C. At the same temperature, a mixture consisting of 400 parts of St, 200 parts of MMA, 200 parts of BA, 200 parts of GMA, 15 parts of AIBN, and 5 parts of TBPO was added dropwise in 5 hr. Furthermore, it was kept at the same temperature for 12 hr. The polymerization was continued, and an acryl copolymer with a nonvolatile matter content of 42.5 % and a viscosity of X was obtained. Next, to this copolymer, 200 parts of soybean oil fatty acid and 100 parts of coconut oil fatty acid were added. At 150°C, the reaction was carried out until the acid value was about 1. A transparent resin solution with a nonvolatile matter content of 50.4 %, a viscosity of Y-Z, an acid value of 1.2, a color number of 3, and a number average molecular weight of 6000 was obtained.

To the resin solution obtained in this manner, 6 % cobalt naphthenate was added at 0.2 % (the solid content ratio) and 24 % lead naphthenate was added at 0.4 % (the solid content ratio). Furthermore, a material by the equivalent addition of Pernock [transliteration] DN-950 (a hexamethylene diisocyanate type curing agent manufactured by Dai Nippon Ink Chemical Ind.

Co., Ltd.) to the coating material after the addition of the dryer in Application Example 1, was also prepared.

As a comparative example, the commercial vinyl acetate-acryl type primer was used.

In regard to the permeation characteristics in the test item, 1 g of a solution diluted to a nonvolatile matter content of 30 % with xylene was added dropwise onto a commercial slate plate and the permeation depth was investigated. For the water resistance and the alkali resistance, the slate plates were subjected to spray coating and dried for one week, dipped in tap water and a saturated calcium hydroxide aqueous solution for two days, and the coated surfaces were evaluated. For the solvent resistance, the slate plate was subjected to spray coating, toluene was spotted after one day, and the coated surface was evaluated.

The results are shown in Table 1.

Table 1

	① 実 施 例				② 比 較 例
	1	2	3	3	市販ビーク リルシーラー
③ 硬化形式	④ ドライヤー イソシアネート用	⑤ ド ラ イ ー 硬 化			⑥ ラッカー乾燥
⑦ 浸透性(mm)	2	2	1.5	1.5~2	0~0.5
⑧ 耐水性	良 ⑨ 好	良 ⑨ 好	良 ⑨ 好	良 ⑨ 好	ブリスダ ⑩
⑪ 耐アルカリ性	良 好	良 好	良 好	良 好	ブリスダ ⑩
⑫ 耐溶剤性	良 好	良 好	良 好	良 好	溶 解 ⑬
⑭ 市販のエマルジョ ンボディとの接着	良 好	良 好	良 好	良 好	容易に剥離 ⑮

- Key: 1 Application Example
 2 Comparative Example (commercial vinyl acetate-acryl type sealer)
 3 Curing mode
 4 Dryer and isocyanate used in combination
 5 Dryer curing
 6 Lacquer drying
 7 Permeation characteristics (mm)
 8 Water resistance
 9 Good
 10 Blister
 11 Alkali resistance
 12 Solvent resistance
 13 Dissolved
 14 Adherence with the commercial emulsion body
 15 Peeled off easily

(2) Application examples and comparative examples related to the top coat

Application Example 4

In a 4-neck flask provided with a thermometer, a reflux cooler, a stirrer and a nitrogen gas inlet, 800 parts of xylene, 71 parts of "Beckosol [transliteration] P-470-70" and 2 parts of DTBPO were charged and heated to 125°C. When the same temperature was reached, a mixture consisting of 400 parts of St, 300 parts of BA, 55 parts of AN, 125 parts of GMA, 70 parts of MMA, 10 parts of AIBN, 7 parts of TBPO, and 4 parts of TBPB was added dropwise in 5 hr. After the completion of the dropwise addition, it was kept at the same temperature for 5 hr. When the nonvolatile matter content was 53.9 %, 200 parts of soybean oil fatty acid and 0.2 parts of 2MIZ were added. At the same temperature, the addition reaction of the glycidyl group and the carboxyl group was carried out for 13 hr. A solution of a fatty acid modified acryl copolymer with a nonvolatile matter content of 60.3 %, a viscosity of Z_3 , and an acid value of 2.6 was obtained. The nonvolatile matter content was adjusted to 50 % by the addition of 400 parts of xylene to this material.

The resin solution obtained in this manner was a transparent solution with a nonvolatile matter content of 50.1 %, a viscosity of V , and a color number of 5-6.

Application Example 5

In the same flask as that in Application Example 1, 200 parts of "Beckosol 1343," 1300 parts of xylene, and 3 parts of DTBPO were charged and heated to 120°C. At the same temperature, a mixture consisting of 300 parts of St, 100 parts of MMA, 200 parts of GMA, 300 parts of EA, 15 parts of AIBN, 10 parts of TBPO, and 2 parts of TBPB was added dropwise in 5 hr. Furthermore, it was kept at the same temperature for 12 hr. The polymerization was continued, and an acryl copolymer with a nonvolatile matter content of 42.0 % and a viscosity of U was obtained.

Next, to this copolymer, 250 parts of coconut oil fatty acid, 100 parts of stearic acid and 50 parts of dehydrated castor oil fatty acid were added. At 150°C, the reaction was carried out until the acid value was about 1. A transparent solution with a nonvolatile matter content of 50.8 %, a viscosity of $X-Y$, an acid value of 1.1, and a color number of 1-2 was obtained.

Next, 120 parts of the varnish obtained in Application Example 4 or 5 and 40 parts of "Taibake [transliteration] CR-90" (titanium oxide, manufactured by Ishihara Ind. Co., Ltd.) were kneaded in a sand mill. A white coating material with PWC 40 % was obtained. To these, 1 part of 6 % cobalt naphthenate, 2 parts of 24 % lead naphthenate, and 1 part of a skin tension inhibitor were added. To a half of the coating material, 10 parts of Pernock [transliteration] DN-950 were further added.

For comparison, the commercial vinyl acetate-acryl type exterior coating material and the commercial acryl urethane type exterior coating material were used.

These coating materials were diluted with a urethane use thinner and sprayed on commercial slate plates and polished mild steel plates. After they had been dried at room temperature for one week, the general physical property tests were carried out. Furthermore, weatherability was judged from the gloss retention ratio after exposure in a border [illegible] district for one year. The results are shown in Table 2.

Table 2

		① 実 施 例			② 比 較 例	
		4	4 / 硬化剤 ③	5	市販ビーク アクリル塗料 ④	市販アクリル ウレタン塗料 ⑤
⑥ 磨き鉄板	光 ⑦ 沢 (60°)	92	92	93	65	90
	エリクセン (mm) ⑧	>7	>7	>7	5	>7
	300g x 1/2 inch 衝撃 (cm) ⑨	>50	>50	>50	20	>50
	硬 度 ⑩	HB	F	HB	B	HB
⑪ スレート板	光 ⑦ 沢 (60°)	70	72	70	45	65
	ゴベン目密着 ⑫	25/25	25/25	25/25	10/25	25/25
	耐 候 性 ⑬	○	◎	○	×	◎
⑭	伸 び	○	○	◎	×	◎
⑮	抗 張 力	○	○	◎	×	◎

- Key:
- 1 Application Example
 - 2 Comparative Example
 - 3 Curing agent
 - 4 Commercial vinyl acetate-acryl coating material
 - 5 Commercial acryl urethane coating material
 - 6 Polished mild steel plates
 - 7 Gloss (60°)
 - 8 Erickson [transliteration] (mm)
 - 9 300 g x 1/2 inch impact (cm)
 - 10 Hardness
 - 11 Slate plates
 - 12 Checkerboard squares adherence
 - 13 Weatherability
 - 14 Elongation
 - 15 Tensile strength